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PATENT ABSTRACTS OF JAPAN

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(54) SOLID ELECTROLYTIC SECONDARY BATTERY

(57)Abstract:
PURPOSE: To enhance charge-discharge cycle characteristic by using a polymer solid electrolyte or polymer gelled electrolyte difficult to react with a negative electrode, and making the internal resistance difficult to rise even by the repeat of charge-discharge cycle.
CONSTITUTION: This solid electrolytic secondary battery has a positive electrode, a negative electrode using lithium as an active material, and a polymer solid electrolyte consisting of a composite of an electrolyte salt with a polymer or a polymer gelled electrolyte obtained by impregnating the polymer with an electrolyte consisting of the electrolyte salt and an aprotic solvent. The polymer is a multiple copolymer of at least three kinds of monomers selected from the group consisting of ethylene oxide, acrylonitrile, epoxy, vinylidene fluoride, ethylene, styrene, urethane, siloxane, and phosphazene.

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(54)【発明の名称】　固体電解質二次電池

(57)【要約】

【構成】正極と、リチウムを活物質とする負極と、電解質塩及び高分子重合体の複合体からなる高分子固体電解質、又は、高分子に電解質塩と非プロトン性溶媒とからなる電解液を含浸させてなる高分子ゲル状電解質とを備える固体電解質二次電池であって、前記高分子重合体が、エチレンオキシド、アクリロニトリル、エポキシ、フッ化ビニリデン、エチレン、スチレン、ウレタン、シロキサン及びフォスファゼンよりなる群から選ばれた少なくとも3種の単量体の多元共重合体である。

【効果】使用せる高分子固体電解質又は高分子ゲル状電解質が負極と反応しにくく、充放電サイクルを繰り返しても内部抵抗が上昇しにくいので、充放電サイクル特性に優れる。

【特許請求の範囲】

【請求項1】正極と、リチウムを活物質とする負極と、電解質塩及び高分子の複合体からなる高分子固体電解質とを備える固体電解質二次電池であって、前記高分子が、エチレンオキシド、アクリロニトリル、エポキシ、フッ化ビニリデン、エチレン、スチレン、ウレタン、シロキサン、スルホン及びフォスファゼンよりなる群から選ばれた少なくとも3種の単量体の多元共重合体であることを特徴とする固体電解質二次電池。

【請求項2】正極と、リチウムを活物質とする負極と、高分子に電解質塩と非プロトン性溶媒とからなる電解液を含浸させてなる高分子ゲル状電解質とを備える固体電解質二次電池であって、前記高分子が、エチレンオキシド、アクリロニトリル、エポキシ、フッ化ビニリデン、エチレン、スチレン、ウレタン、シロキサン、スルホン及びフォスファゼンよりなる群から選ばれた少なくとも3種の単量体の多元共重合体であることを特徴とする固体電解質二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は固体電解質二次電池に係わり、詳しくは充放電サイクル特性に優れた固体電解質二次電池を得ることを目的とした、高分子固体電解質又は高分子ゲル状電解質の改良に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】近年、固体電解質電池が、漏液の心配が無いためにポジションフリーであること、電解液の注液を必要としないために電池の組立が容易であることなどの液体電解質電池には無い利点があることから、注目されている。

【0003】而して、その電解質としては、$LiClO_4$、$LiBF_4$等の電解質塩とPEO（ポリエチレンオキシド）とを複合化した高分子固体電解質が提案されている。

【0004】しかしながら、PEOを用いた高分子固体電解質は、充放電サイクルを繰り返すと、PEOが負極のリチウムと反応し、両者の界面に電子伝導性の無いLi_2O等の被膜が生成するため、従来提案されている固体電解質二次電池には、充放電サイクル特性が良くないという問題があった。このため、現在実用化されている固体電解質電池は、心臓ペースメーカーの電源用に使用されているリチウム電池（一次電池）のみである。

【0005】本発明は、上述の問題を解決するべくなされたものであって、その目的とするところは、充放電サイクル特性に優れた固体電解質二次電池を提供するにある。

【0006】

【課題を解決するための手段】上記目的を達成するための請求項1記載の発明に係る固体電解質電池（以下、「第1電池」と称する。）は、正極と、リチウムを活物質とする負極と、電解質塩及び高分子の複合体からなる高分子固体電解質とを備える固体電解質二次電池であって、前記高分子が、エチレンオキシド、アクリロニトリル、エポキシ、フッ化ビニリデン、エチレン、スチレン、ウレタン、シロキサン、スルホン及びフォスファゼンよりなる群から選ばれた少なくとも3種の単量体の多元共重合体であるものである。

【0007】また、請求項2記載の発明に係る固体電解質電池（以下、「第2電池」と称する。）は、正極と、リチウムを活物質とする負極と、高分子に電解質塩と非プロトン性溶媒とからなる電解液を含浸させてなる高分子ゲル状電解質とを備える固体電解質二次電池であって、前記高分子が、エチレンオキシド、アクリロニトリル、エポキシ、フッ化ビニリデン、エチレン、スチレン、ウレタン、シロキサン、スルホン及びフォスファゼンよりなる群から選ばれた少なくとも3種の単量体の多元共重合体であるものである。なお、高分子ゲル状電解質を用いた電池は、厳密にはゲル状電解質電池と称すべきかも知れないが、高分子ゲル状電解質は見掛け上固形であるので、本明細書ではこれをも固体電解質電池に含める。また、第1電池と第2電池とを本発明電池と総称することがある。

【0008】第1電池は、電解質として電解質塩と特定の多元共重合体との複合体からなる高分子固体電解質を用いた固体電解質電池であり、また第2電池は、電解質として電解質塩と非プロトン性溶媒とからなる電解液を特定の多元共重合体に含浸させてなる高分子ゲル状電解質を用いた固体電解質電池である。

【0009】本発明電池におけるリチウムを活物質とする負極としては、金属リチウム又はリチウムを吸蔵放出可能な、合金、酸化物、炭素材料が例示される。リチウムを吸蔵放出可能な合金としては、リチウム－アルミニウム合金、リチウム－インジウム合金、リチウム－錫合金、リチウム－鉛合金、リチウム－ビスマス合金、リチウム－ガリウム合金、リチウム－亜鉛合金、リチウム－カドミウム合金、リチウム－珪素合金、リチウム－カルシウム合金、リチウム－バリウム合金、リチウム－ストロンチウム合金が、リチウムを吸蔵放出可能な酸化物としては、酸化鉄、酸化錫、酸化ニオビウム、酸化タングステン、酸化チタンが、またリチウムを吸蔵放出可能な炭素材料としては、コークス、黒鉛、有機物焼成体が、それぞれ例示される。

【0010】本発明電池における正極の活物質は特に制限されず、例えばマンガン、コバルト、ニッケル、バナジウム及びニオブから選ばれた少なくとも1種の金属を含有する金属酸化物が挙げられる。

【0011】本発明電池における多元共重合体の具体例としては、エチレンオキシド－アクリロニトリル－エポキシ3元共重合体、エチレンオキシド－フッ化ビニリデン－エチレン3元共重合体、フォスファゼン－スチレン

ーシロキサン3元共重合体、ウレタン−エチレンオキシド−スチレン3元共重合体、エチレンオシキド−フォスファゼン−スチレン3元共重合体、エチレンオシキド−フォスファゼン−スルホン3元共重合体が例示される。

【0012】本発明電池における電解質塩としては、過塩素酸リチウム（$LiClO_4$）、トリフルオロメタンスルホン酸リチウム（$LiCF_3SO_3$）、六フッ化リン酸リチウム（$LiPF_6$）、四フッ化ホウ酸リチウム（$LiBF_4$）、六フッ化ヒ酸リチウム（$LiAsF_6$）、六フッ化アンチモン酸リチウム（$LiSbF_6$）、リチウムトリフルオロメタンスルホン酸イミド［$LiN(CF_3SO_2)_2$］が例示される。

【0013】第2電池における非プロトン性溶媒としては、エチレンカーボネート（EC）、プロピレンカーボネート（PC）、ブチレンカーボネート（BC）、γ−ブチロラクトン（γ−BL）、スルホラン（SL）、1，2−ジメトキシエタン（DME）、1，2−ジエトキシエタン（DEE）、エトキシメトキシエタン（EMC）、テトラヒドロフラン（THF）、2−メチルテトラヒドロフラン（2M−THF）、1，3−ジオキソラン（DOXL）、4−メチル−1，3−ジオキソラン（4M−DOXL）が例示される。

【0014】

【作用】充放電サイクルを繰り返しても内部抵抗が上昇しにくいので、従来の固体電解質電池と比較して、放電容量が低下しにくい。負極と高分子固体電解質又は高分子ゲル状電解質とが反応しにくく、それゆえ両者の界面に電子伝導性の無いLi_2O等の被膜が生成しにくいためと推察される。

【0015】

*【実施例】以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は下記実施例に何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

【0016】（実施例1〜6：第1電池）

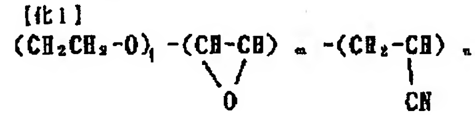
〔正極〕正極活物質としての二酸化マンガンと、導電剤としての黒鉛粉末と、PTFE（ポリテトラフルオロエチレン）とを重量比8：1：1で混合して正極合剤を調製し、これを円板状に成形し、100°Cで真空乾燥して、正極を作製した。

【0017】〔負極〕リチウム−アルミニウム合金を用いた。

【0018】〔高分子固体電解質〕化1〜化6に構造式を示す平均分子量約6万の各種の3元共重合体93重量部を、アセトニトリルに溶かして溶液を調製し、この溶液に$LiClO_4$ 7重量部を加えて混合し、これをステンレス製のシャーレ上にキャストし、減圧乾燥してアセトニトリルを除去した後、100°Cで加熱乾燥して、高分子固体電解質を作製した。実施例1〜6で使用した3元共重合体は化1〜化6中のnとmとlが1：1：1の比率のものである。

【0019】

【化1】



【0020】

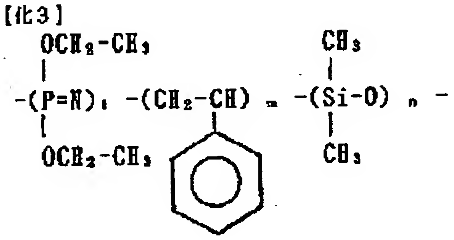
【化2】

*

$$-(CH_2CH_2-O)_n-(CH_2-CF_2)_m-(CH_2-CH_2)_l-$$

【0021】

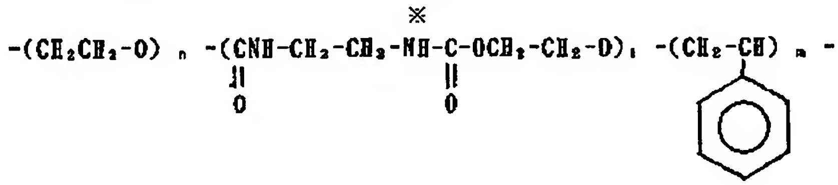
【化3】



※【0022】

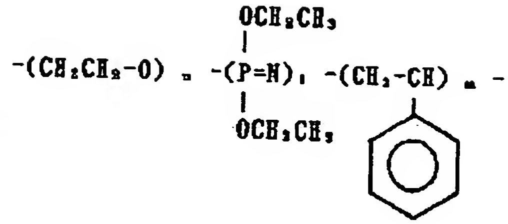
【化4】

※



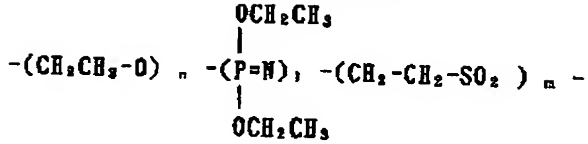
【0023】

【化5】



【0024】

＊　＊【化6】



【0025】〔固体電解質電池〕上記の正極、負極及び各高分子固体電解質を用いて、順に、扁平型の固体電解質電池Ａ１～Ａ６（第１電池；理論容量：３０ｍＡｈ／ｇ－電池重量；電池寸法：直径２０ｍｍ、厚さ１．６ｍｍ）を組み立てた。

【００２６】（実施例７～１２：第２電池）表２に示す各種の３元共重合体フィルムを、プロピレンカーボネートに$LiClO_4$を１モル／リットル溶かした溶液（電解液）に浸漬して膨潤させ、高分子ゲル状電解質を作製した。なお、含浸せる電解液と各フィルムとの重量比は全て４：１とした。次いで、これらの高分子ゲル状電解質を用いたこと以外は実施例１～６と同様にして、固体電解質電池Ａ７～Ａ１２（第２電池）を組み立てた。

【００２７】（比較例１）平均分子量約６万のポリエチレンオキシド〔$-(CH_2-CH_2-O)_n-$〕９３重量部を、アセトニトリルに溶かして溶液を調製し、この溶液に$LiClO_4$ ７重量部を加え、これをステンレス製のシャーレ上にキャストし、減圧乾燥してアセトニトリルを除去した後、１００°Ｃで加熱乾燥して、高分子固体電解質を作製した。この高分子固体電解質を用いたこと以外は実施例１～６と同様にして、固体電解質電池Ｂ１を組み立てた。

【００２８】（比較例２～４）$LiClO_4$を、エチレンカーボネートと１，２－ジメトキシエタンとの体積比３：２の混合溶媒（比較例２）、エチレンカーボネートとテトラヒドロフランとの体積比３：２の混合溶媒（比較例３）又はエチレンカーボネートと１，２－ジメトキシエタンとテトラヒドロフランとの体積比３：１：１の混合溶媒（比較例４）に１モル／リットル溶かした溶液を電解液として用いて、順に液体電解質電池Ｂ２～Ｂ４を組み立てた。セパレータとしては、ポリプロピレン製の不織布を用いた。

【００２９】（比較例５）ポリエチレンオキシドフィルムを、プロピレンカーボネートに$LiClO_4$を１モル／リットル溶かした溶液（電解液）に浸漬して膨潤させ、高分子ゲル状電解質を作製した。なお、含浸せる電解液とポリエチレンオキシドフィルムとの重量比は全て４：１とした。次いで、この高分子ゲル状電解質を用いたこと以外は実施例１～６と同様にして、固体電解質電池Ｂ５を組み立てた。

【００３０】（分解電流）各電解質と、作用極としての白金電極と、対極及び参照極としてのリチウム電極とを用いて、試験セルを組み立て、次いで白金電極の電位を０Ｖ対参照極（Li/Li^+）に設定したときの還元電流（分解電流$\mu A/cm^2$）を測定して、各電解質の分解性の難易を調べた。分解電流が大きいほど、電解質が分解し易いことを表す。結果を表１及び表２に示す。

【００３１】

【表１】

電池	高分子　又は溶媒	分解電流 (μA/cm²)	50ｻｲｸﾙ目の放電容量 (mAh／g)
A 1	ｴﾁﾚﾝｵｷｼﾄﾞ-ｱｸﾘﾛﾆﾄﾘﾙ-ｴﾎﾟｷｼ	5．3	22
A 2	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｯ化ﾋﾞﾆﾘﾃﾞﾝ-ｴﾁﾚﾝ	5．2	21
A 3	ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ-ｸﾛﾛｷｼﾝ	5．0	25
A 4	ｳﾚﾀﾝ-ｴﾁﾚﾝｵｷｼﾄﾞ-ｽﾁﾚﾝ	4．9	20
A 5	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ	5．0	24
A 6	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾙﾎﾝ	4．5	19
B 1	ﾎﾟﾘｴﾁﾚﾝｵｷｼﾄﾞ	15．2	10
B 2	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+1,2-ｼﾞﾒﾄｷｼｴﾀﾝ	20．4	10
B 3	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+ﾃﾄﾗﾋﾄﾞﾛﾌﾗﾝ	21．4	8
B 4	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+1,2-ｼﾞﾒﾄｷｼｴﾀﾝ+ﾃﾄﾗﾋﾄﾞﾛﾌﾗﾝ	23．2	7

【0032】

＊　＊【表2】

電池	高分子	電解液	分解電流 (μA/cm²)	50ｻｲｸﾙ目の放電容量 (mAh／g)
A 7	ｴﾁﾚﾝｵｷｼﾄﾞ-ｱｸﾘﾛﾆﾄﾘﾙ-ｴﾎﾟｷｼ	$LiClO_4$+PC	5．8	25
A 8	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｯ化ﾋﾞﾆﾘﾃﾞﾝ-ｴﾁﾚﾝ	$LiClO_4$+PC	5．8	26
A 9	ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ-ｸﾛﾛｷｼﾝ	$LiClO_4$+PC	5．5	26
A10	ｳﾚﾀﾝ-ｴﾁﾚﾝｵｷｼﾄﾞ-ｽﾁﾚﾝ	$LiClO_4$+PC	5．4	27
A11	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ	$LiClO_4$+PC	5．3	28
A12	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾙﾎﾝ	$LiClO_4$+PC	5．0	27
B 5	ﾎﾟﾘｴﾁﾚﾝｵｷｼﾄﾞ	$LiClO_4$+PC	18．2	11

【0033】表1より、実施例1～6で作製した高分子固体電解質は、比較例2～4で作製した液体電解質はもとより、比較例1で作製した従来の高分子固体電解質と比較して、分解電流が小さいことから、分解しにくいことが分かる。また、表2より、実施例7～12で作製した高分子ゲル状電解質は、比較例5で作製した従来の高分子ゲル状電解質と比較して、分解電流が小さいことから、分解しにくいことが分かる。

【0034】（50サイクル目の放電容量）各電池について、室温（25°C）下にて、0．5mA／cm² で3．20Vまで充電した後、0．5mA／cm² で2．00Vまで放電する工程を1サイクルとする充放電サイクル試験を行い、50サイクル目の放電容量を求めた。※※結果を先の表1及び表2に示す。

【0035】表1及び表2より、分解電流が小さい高分子固体電解質又は高分子ゲル状電解質を用いた固体電解質電池A1～A12（本発明電池）は、分解電流が大きい高分子固体電解質、液体電解質又は高分子ゲル状電解質を用いた電池B1～B5（比較電池）に比し、50サイクル目の放電容量が大きく、充放電サイクル特性に優れていることが分かる。

【0036】

【発明の効果】使用せる高分子固体電解質又は高分子ゲル状電解質が負極と反応しにくく、充放電サイクルを繰り返しても内部抵抗が上昇しにくいので、充放電サイクル特性に優れる。

フロントページの続き

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CLAIMS

[Claim(s)]

[Claim 1] The solid electrolyte rechargeable battery characterized by being a solid electrolyte rechargeable battery equipped with a positive electrode, the negative electrode which makes a lithium an active material, and the solid polymer electrolyte which consists of an electrolyte salt and complex of a macromolecule, and being the plural copolymers of at least three sorts of monomers chosen from the group which the aforementioned macromolecule becomes from ethylene oxide, acrylonitrile, epoxy, a fluoride vinylidene, ethylene, styrene, urethane, a siloxane, a sulfone, and force FAZEN.

[Claim 2] The solid electrolyte rechargeable battery characterized by being a solid electrolyte rechargeable battery equipped with a positive electrode, the negative electrode which makes a lithium an active material, and the macromolecule gel electrolyte into which make the electrolytic solution which becomes a macromolecule from an electrolyte salt and an aprotic solvent come to sink, and being the plural copolymers of at least three sorts of monomers chosen from the group which the aforementioned macromolecule becomes from ethylene oxide, acrylonitrile, epoxy, a fluoride vinylidene, ethylene, styrene, urethane, a siloxane, a sulfone, and force FAZEN.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to improvement of the solid polymer electrolyte aiming at obtaining the solid electrolyte rechargeable battery excellent in the charge-and-discharge cycle property in detail with respect to a solid electrolyte rechargeable battery, or a macromolecule gel electrolyte.
[0002]
[Description of the Prior Art] It is observed from there being an advantage which is not in liquid electrolyte cells, like the assembly of a cell is easy, since a solid electrolyte cell does not need that it is a position free-lancer in order that there may be no worries about a liquid spill, and the clysis of the electrolytic solution in recent years.
[0003] **(ing) -- as the electrolyte -- $LiClO_4$ and $LiBF_4$ etc. -- the solid polymer electrolyte which composite-ized an electrolyte salt and PEO (polyethylene oxide) is proposed
[0004] However, when the charge-and-discharge cycle was repeated, PEO reacted with the lithium of a negative electrode, and the solid polymer electrolyte using PEO had the problem that a charge-and-discharge cycle property was not good in the solid electrolyte rechargeable battery by which the conventional proposal is made, in order that coats, such as Li_2O which does not have electronic-conduction nature in both interface, might generate. For this reason, the solid electrolyte cell put in practical use now is only a lithium cell (primary cell) currently used for the power supplies of an artificial cardiac pacemaker.
[0005] The place which this invention is made to solve an above-mentioned problem, and is made into the purpose is to offer the solid electrolyte rechargeable battery excellent in the charge-and-discharge cycle property.
[0006]
[Means for Solving the Problem] The solid electrolyte cell concerning invention according to claim 1 for attaining the above-mentioned purpose ("the 1st cell" is called hereafter.) It is a solid electrolyte rechargeable battery equipped with a positive electrode, the negative electrode which makes a lithium an active material, and the solid polymer electrolyte which consists of an electrolyte salt and complex of a macromolecule, and they are the plural copolymers of at least three sorts of monomers chosen from the group which the aforementioned macromolecule becomes from ethylene oxide, acrylonitrile, epoxy, a fluoride vinylidene, ethylene, styrene, urethane, a siloxane, a sulfone, and force FAZEN.
[0007] Moreover, the solid electrolyte cell concerning invention according to claim 2 ("the 2nd cell" is called hereafter.) It is a solid electrolyte rechargeable battery equipped with a positive electrode, the negative electrode which makes a lithium an active material, and the macromolecule gel electrolyte into which make the electrolytic solution which becomes a macromolecule from an electrolyte salt and an aprotic solvent come to sink, and they are the plural copolymers of at least three sorts of monomers chosen from the group which the aforementioned macromolecule becomes from ethylene oxide, acrylonitrile, epoxy, a fluoride vinylidene, ethylene, styrene, urethane, a siloxane, a sulfone, and force FAZEN. In addition, although the cell using the macromolecule gel electrolyte is strictly called a gel electrolyte cell, since a macromolecule gel electrolyte is a solid seemingly, on these specifications, this is also included in a solid electrolyte cell. Moreover, the 1st cell and the 2nd cell may be named this invention cell generically.

[0008] The 1st cell is a solid electrolyte cell using the solid polymer electrolyte which consists of complex of an electrolyte salt and specific plural copolymers as an electrolyte, and the 2nd cell is a solid electrolyte cell using the macromolecule gel electrolyte which makes the electrolytic solution which consists of an electrolyte salt and an aprotic solvent as an electrolyte come to sink into specific plural copolymers.

[0009] As a negative electrode which makes the lithium in this invention cell an active material, the alloy and oxide which can occlusion emit a metal lithium or a lithium, and a carbon material are illustrated. As an alloy which can occlusion emit a lithium, a lithium-aluminium alloy, A lithium-indium alloy, a lithium-tin alloy, a lithium-lead alloy, A lithium-bismuth alloy, a lithium-gallium alloy, a lithium-zinc alloy, A lithium-cadmium alloy, a lithium-silicon alloy, a lithium-calcium alloy, A lithium-barium alloy and a lithium-strontium alloy as an oxide which can occlusion emit a lithium As a carbon material [an iron oxide, a tin oxide, an oxidization niobium, a tungstic oxide, and titanium oxide] which can occlusion emit a lithium again, corks, a graphite, and an organic substance baking object are illustrated, respectively.

[0010] The metallic oxide containing at least one sort of metals which especially the active material of the positive electrode in this invention cell was not restricted, for example, were chosen from manganese, cobalt, nickel, vanadium, and niobium is mentioned.

[0011] As an example of the plural copolymers in this invention cell, ethylene oxide-acrylonitrile-epoxy the copolymer of 3 yuan, ethylene oxide-fluoride vinylidene-ethylene the copolymer of 3 yuan, force FAZEN-styrene-siloxane the copolymer of 3 yuan, urethane-ethylene oxide-styrene the copolymer of 3 yuan, ethylene OSHIKIDO-force FAZEN-styrene the copolymer of 3 yuan, and ethylene OSHIKIDO-force FAZEN-sulfone the copolymer of 3 yuan are illustrated.

[0012] As an electrolyte salt in this invention cell, a lithium perchlorate ($LiClO_4$), a trifluoromethane sulfonic-acid lithium ($LiCF_3SO_3$), a 6 fluoride [phosphoric-acid] lithium ($LiPF_6$), 4 fluoride lithium borate ($LiBF_4$), a 6 fluoride [arsenic acid] lithium ($LiAsF_6$), an antimony hexafluoride acid lithium ($LiSbF_6$), and lithium trifluoromethane sulfonic-acid imide [$LiN(CF_3SO_2)_2$] are illustrated.

[0013] As an aprotic solvent in the 2nd cell Ethylene carbonate (EC), propylene carbonate (PC), Butylene carbonate (BC), gamma-butyrolactone (gamma-BL), A sulfolane (SL), 1, 2-dimethoxyethane (DME), 1, 2-diethoxy ethane (DEE), Ethoxy methoxyethane (EMC), a tetrahydrofuran (THF), 2-methyl tetrahydrofuran (2 M-THF), 1, 3-dioxolane (DOXL), the 4-methyl -1, and 3-dioxolane (4 M-DOXL) are illustrated.

[0014]

[Function] Since internal resistance cannot rise easily even if it repeats a charge-and-discharge cycle, as compared with the conventional solid electrolyte cell, service capacity cannot fall easily. A negative electrode, a solid polymer electrolyte, or a macromolecule gel electrolyte cannot react easily, and it guesses to be hard to generate coats, such as Li_2O which so does not have electronic-conduction nature in both interface.

[0015]

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0016] (An example 1 - 6 : the 1st cell)

a [positive electrode] -- manganese dioxide as a positive active material, the graphite powder as an electric conduction agent, and PTFE (polytetrafluoroethylene) -- the weight ratio 8:1:1 -- mixing -- a positive electrode -- the mixture was prepared, this was fabricated to disc-like, the vacuum drying was carried out by 100 degreeC, and the positive electrode was produced

[0017] [Negative electrode] The lithium-aluminium alloy was used.

[0018] [Solid polymer electrolyte] After melted to the acetonitrile various kinds of 3 yuan copolymer 93 weight sections of the average molecular weight 60,000 [about] which shows a structure expression to-izing 1 --izing 6, prepared the solution, added the $LiClO_4$ 7 weight section to this solution, having mixed, having carried out the cast of this, having carried out reduced pressure drying on the petri dish made from stainless steel and removing an acetonitrile, stoving was carried out by 100 degreeC and the solid polymer electrolyte was produced. The 3 yuan copolymer used in the

examples 1-6 is the thing of n under ** 1 --izing 6, and the ratio of m and l1:1:1.

[0019]

[Formula 1]

$$(CH_2CH_2-O)_l-(\underset{\diagdown O \diagup}{CH-CH})_m-(CH_2-\underset{|\atop CN}{CH})_n$$

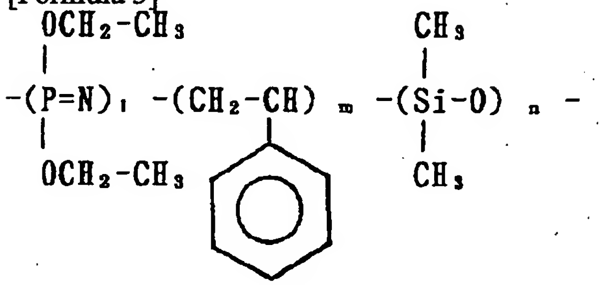
[0020]

[Formula 2]

$$-(CH_2CH_2-O)_n-(CH_2-CF_2)_m-(CH_2-CH_2)_l-$$

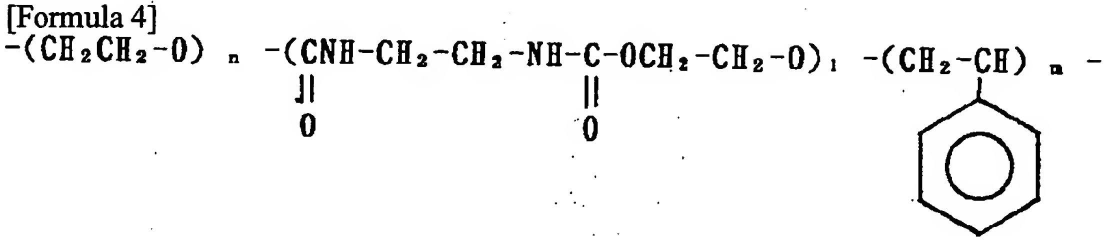
[0021]

[Formula 3]



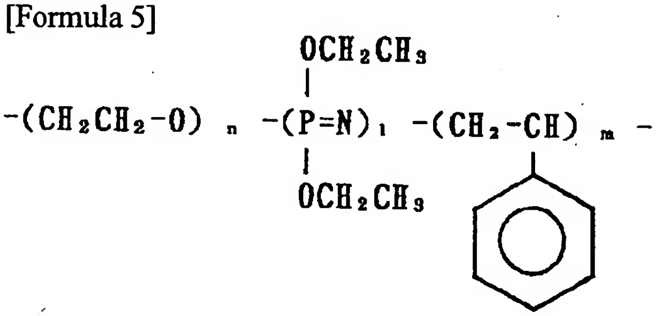
[0022]

[Formula 4]



[0023]

[Formula 5]



[0024]

[Formula 6]

$$-(CH_2CH_2-O)_n-(\overset{OCH_2CH_3\atop |}{\underset{|\atop OCH_2CH_3}{P}}=N)_l-(CH_2-CH_2-SO_2)_m-$$

[0025] [Solid electrolyte cell] The flat type solid electrolyte cells A1-A6 (1st cell; geometric capacity : 30 mAh/g-cell weight; cell size : 1.6mm in the diameter of 20mm, thickness) were assembled in order using a positive electrode, an above-mentioned negative electrode, and each above-mentioned solid polymer electrolyte.

[0026] (An example 7 - 12 : the 2nd cell) They are various kinds of 3 yuan copolymer films shown in

Table 2 to propylene carbonate LiClO4 Flood with the solution (electrolytic solution) melted l. one mol /, it was made to swell, and the macromolecule gel electrolyte was produced. In addition, all the weight ratios of the sinking-in **** electrolytic solution and each film were set to 4:1. Subsequently, solid electrolyte cells A7-A12 (the 2nd cell) were assembled like examples 1-6 except having used these macromolecule gel electrolytes.

[0027] (Example 1 of comparison) After melted the polyethylene-oxide [-(CH2-CH2-O) n-] 93 weight section of average molecular weight 60,000 [about] to the acetonitrile, prepared the solution, having added the LiClO4 7 weight section to this solution, having carried out the cast of this, having carried out reduced pressure drying on the petri dish made from stainless steel and removing an acetonitrile, stoving was carried out by 100 degreeC and the solid polymer electrolyte was produced. The solid electrolyte cell B1 was assembled like examples 1-6 except having used this solid polymer electrolyte.

[0028] (Examples 2-4 of comparison) LiClO4 Mixed solvent of the volume ratio 3:2 of ethylene carbonate and 1 and 2-dimethoxyethane (example 2 of comparison), Liquid electrolyte cell B-2-B4 were assembled in order to the mixed solvent (example 4 of comparison) of the volume ratio 3:1:1 of the mixed solvent (example 3 of comparison) of the volume ratio 3:2 of ethylene carbonate and a tetrahydrofuran or ethylene carbonate, 1 and 2-dimethoxyethane, and a tetrahydrofuran, using the solution melted l. one mol /as the electrolytic solution. The nonwoven fabric made from polypropylene was used as separator.

[0029] (Example 5 of comparison) It is a polyethylene-oxide film to propylene carbonate LiClO4 Flood with the solution (electrolytic solution) melted l. one mol /, it was made to swell, and the macromolecule gel electrolyte was produced. In addition, all the weight ratios of the sinking-in **** electrolytic solution and a polyethylene-oxide film were set to 4:1. Subsequently, solid-electrolyte-cell B5 was assembled like examples 1-6 except having used this macromolecule gel electrolyte.

[0030] <Decomposition current> Using each electrolyte, the platinum electrode as an operation pole, and the lithium electrode as a counter electrode and a reference pole, the examination cell was assembled, the reduction current (decomposition current muA/cm2) when subsequently to 0 V pair reference pole (Li/Li+) setting up the potential of a platinum electrode was measured, and the difficulty of the resolvability of each electrolyte was investigated. It means that it is easy to disassemble an electrolyte, so that decomposition current is large. A result is shown in Table 1 and 2.

[0031]

[Table 1]

電池	高分子　又は溶媒	分解電流 (μA/cm²)	50ｻｲｸﾙ目の放電容量 (mAh/g)
A 1	ｴﾁﾚﾝｵｷｼﾄﾞ-ｱｸﾘﾛﾆﾄﾘﾙ-ｴﾎﾟｷｼ	5.3	22
A 2	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｯ 化ﾋﾞﾆﾘﾃﾞﾝ-ｴﾁﾚﾝ	5.2	21
A 3	ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ-ｼﾛｷｻﾝ	5.0	25
A 4	ｳﾚﾀﾝ-ｴﾁﾚﾝｵｷｼﾄﾞ-ｽﾁﾚﾝ	4.9	20
A 5	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ	5.0	24
A 6	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾙﾎﾝ	4.5	19
B 1	ﾎﾟﾘｴﾁﾚﾝｵｷｼﾄﾞ	15.2	10
B 2	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+1,2-ｼﾞﾒﾄｷｼｴﾀﾝ	20.4	10
B 3	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+ﾃﾄﾗﾋﾄﾞﾛﾌﾗﾝ	21.4	8
B 4	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+1,2-ｼﾞﾒﾄｷｼｴﾀﾝ +ﾃﾄﾗﾋﾄﾞﾛﾌﾗﾝ	23.2	7

[0032]

[Table 2]

電池	高分子	電解液	分解電流 (μA/cm²)	50ｻｲｸﾙ目の放電容量 (mAh／g)
A 7	ｴﾁﾚﾝｵｷｼﾄﾞ-ｱｸﾘﾛﾆﾄﾘﾙ-ｴﾎﾟｷｼ	$LiClO_4$+PC	5．8	25
A 8	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｯ 化ﾋﾞﾆﾘﾃﾞﾝ-ｴﾁﾚﾝ	$LiClO_4$+PC	5．8	26
A 9	ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ-ｼﾛｷｻﾝ	$LiClO_4$+PC	5．5	25
A 10	ｳﾚﾀﾝ-ｴﾁﾚﾝｵｷｼﾄﾞ-ｽﾁﾚﾝ	$LiClO_4$+PC	5．4	27
A 11	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ	$LiClO_4$+PC	5．3	28
A 12	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾙﾎﾝ	$LiClO_4$+PC	5．0	27
B 5	ﾎﾟﾘｴﾁﾚﾝｵｷｼﾄﾞ	$LiClO_4$+PC	18．2	11

[0033] Table 1 shows that it is hard to decompose from decomposition current being small as compared with the conventional solid polymer electrolyte which produced the liquid electrolyte which produced the solid polymer electrolyte produced in the examples 1-6 in the examples 2-4 of comparison in the example 1 of comparison from the first. Moreover, Table 2 shows that it is hard to decompose from decomposition current being small as compared with the conventional macromolecule gel electrolyte which produced the macromolecule gel electrolyte produced in the examples 7-12 in the example 5 of comparison.

[0034] <50 Service capacity of a cycle eye> It is 0.5 mA/cm2 under a room temperature (25degreeC) about each cell. 0.5 mA/cm2 after charging to 3.20V The charge-and-discharge cycle examination which makes 1 cycle the process which discharges to 2.00V was performed, and the service capacity of 50 cycle eye was calculated. A result is shown in previous Table 1 and 2.

[0035] Decomposition current compares the solid electrolyte cells A1-A12 (this invention cell) using the solid polymer electrolyte with decomposition current smaller than Table 1 and 2, or the macromolecule gel electrolyte with the cell B1 using the large solid polymer electrolyte, the liquid electrolyte, or the macromolecule gel electrolyte - B5 (comparison cell), the service capacity of 50 cycle eye is large, and it turns out that it excels in the charge-and-discharge cycle property.

[0036]

[Effect of the Invention] Since internal resistance cannot rise easily even if a use **** solid polymer electrolyte or a macromolecule gel electrolyte cannot react easily with a negative electrode and repeats a charge-and-discharge cycle, it excels in a charge-and-discharge cycle property.

[Translation done.]

* NOTICES *

TECHNICAL FIELD

[Industrial Application] this invention relates to improvement of the solid polymer electrolyte aiming at obtaining the solid electrolyte rechargeable battery excellent in the charge-and-discharge cycle property in detail with respect to a solid electrolyte rechargeable battery, or a macromolecule gel electrolyte.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] Since internal resistance cannot rise easily even if a use **** solid polymer electrolyte or a macromolecule gel electrolyte cannot react easily with a negative electrode and repeats a charge-and-discharge cycle, it excels in a charge-and-discharge cycle property.

[Translation done.]

MEANS

[Means for Solving the Problem] The solid electrolyte cell concerning invention according to claim 1 for attaining the above-mentioned purpose ("the 1st cell" is called hereafter.) It is a solid electrolyte rechargeable battery equipped with a positive electrode, the negative electrode which makes a lithium an active material, and the solid polymer electrolyte which consists of an electrolyte salt and complex of a macromolecule, and they are the plural copolymers of at least three sorts of monomers chosen from the group which the aforementioned macromolecule becomes from ethylene oxide, acrylonitrile, epoxy, a fluoride vinylidene, ethylene, styrene, urethane, a siloxane, a sulfone, and force FAZEN.
[0007] Moreover, the solid electrolyte cell concerning invention according to claim 2 ("the 2nd cell" is called hereafter.) It is a solid electrolyte rechargeable battery equipped with a positive electrode, the negative electrode which makes a lithium an active material, and the macromolecule gel electrolyte into which make the electrolytic solution which becomes a macromolecule from an electrolyte salt and an aprotic solvent come to sink, and they are the plural copolymers of at least three sorts of monomers chosen from the group which the aforementioned macromolecule becomes from ethylene oxide, acrylonitrile, epoxy, a fluoride vinylidene, ethylene, styrene, urethane, a siloxane, a sulfone, and force FAZEN. In addition, although the cell using the macromolecule gel electrolyte is strictly called a gel electrolyte cell, since a macromolecule gel electrolyte is a solid seemingly, on these specifications, this is also included in a solid electrolyte cell. Moreover, the 1st cell and the 2nd cell may be named this invention cell generically.
[0008] The 1st cell is a solid electrolyte cell using the solid polymer electrolyte which consists of complex of an electrolyte salt and specific plural copolymers as an electrolyte, and the 2nd cell is a solid electrolyte cell using the macromolecule gel electrolyte which makes the electrolytic solution which consists of an electrolyte salt and an aprotic solvent as an electrolyte come to sink into specific plural copolymers.
[0009] As a negative electrode which makes the lithium in this invention cell an active material, the alloy and oxide which can occlusion emit a metal lithium or a lithium, and a carbon material are illustrated. As an alloy which can occlusion emit a lithium, a lithium-aluminium alloy, A lithium-indium alloy, a lithium-tin alloy, a lithium-lead alloy, A lithium-bismuth alloy, a lithium-gallium alloy, a lithium-zinc alloy, A lithium-cadmium alloy, a lithium-silicon alloy, a lithium-calcium alloy, A lithium-barium alloy and a lithium-strontium alloy as an oxide which can occlusion emit a lithium As a carbon material [an iron oxide, a tin oxide, an oxidization niobium, a tungstic oxide, and titanium oxide] which can occlusion emit a lithium again, corks, a graphite, and an organic substance baking object are illustrated, respectively.
[0010] The metallic oxide containing at least one sort of metals which especially the active material of the positive electrode in this invention cell was not restricted, for example, were chosen from manganese, cobalt, nickel, vanadium, and niobium is mentioned.
[0011] As an example of the plural copolymers in this invention cell, ethylene oxide-acrylonitrile-epoxy the copolymer of 3 yuan, ethylene oxide-fluoride vinylidene-ethylene the copolymer of 3 yuan, force FAZEN-styrene-siloxane the copolymer of 3 yuan, urethane-ethylene oxide-styrene the copolymer of 3 yuan, ethylene OSHIKIDO-force FAZEN-styrene the copolymer of 3 yuan, and ethylene OSHIKIDO-force FAZEN-sulfone the copolymer of 3 yuan are illustrated.
[0012] As an electrolyte salt in this invention cell, a lithium perchlorate ($LiClO_4$), a trifluoromethane sulfonic-acid lithium ($LiCF_3SO_3$), a 6 fluoride [phosphoric-acid] lithium ($LiPF_6$), 4 fluoride

lithium borate ($LiBF_4$), a 6 fluoride [arsenic acid] lithium ($LiAsF_6$), an antimony hexafluoride acid lithium ($LiSbF_6$), and lithium trifluoromethane sulfonic-acid imide [$LiN(CF_3SO_2)_2$] are illustrated.
[0013] As an aprotic solvent in the 2nd cell Ethylene carbonate (EC), propylene carbonate (PC), Butylene carbonate (BC), gamma-butyrolactone (gamma-BL), A sulfolane (SL), 1, 2-dimethoxyethane (DME), 1, 2-diethoxy ethane (DEE), Ethoxy methoxyethane (EMC), a tetrahydrofuran (THF), 2-methyl tetrahydrofuran (2 M-THF), 1, 3-dioxolane (DOXL), the 4-methyl -1, and 3-dioxolane (4 M-DOXL) are illustrated.

[Translation done.]

OPERATION

[Function] Since internal resistance cannot rise easily even if it repeats a charge-and-discharge cycle, as compared with the conventional solid electrolyte cell, service capacity cannot fall easily. A negative electrode, a solid polymer electrolyte, or a macromolecule gel electrolyte cannot react easily, and it guesses to be hard to generate coats, such as Li2 O which so does not have electronic-conduction nature in both interface.
[0015]

[Translation done.]

* NOTICES *

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EXAMPLE

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0016] (An example 1 - 6 : the 1st cell)

a [positive electrode] -- manganese dioxide as a positive active material, the graphite powder as an electric conduction agent, and PTFE (polytetrafluoroethylene) -- the weight ratio 8:1:1 -- mixing -- a positive electrode -- the mixture was prepared, this was fabricated to disc-like, the vacuum drying was carried out by 100 degreeC, and the positive electrode was produced

[0017] [Negative electrode] The lithium-aluminium alloy was used.

[0018] [Solid polymer electrolyte] After melted to the acetonitrile various kinds of 3 yuan copolymer 93 weight sections of the average molecular weight 60,000 [about] which shows a structure expression to-izing 1 --izing 6, prepared the solution, added the LiClO4 7 weight section to this solution, having mixed, having carried out the cast of this, having carried out reduced pressure drying on the petri dish made from stainless steel and removing an acetonitrile, stoving was carried out by 100 degreeC and the solid polymer electrolyte was produced. The 3 yuan copolymer used in the examples 1-6 is the thing of n under **. 1 --izing 6, and the ratio of m and 11:1:1.

[0019]

[Formula 1]

$$(CH_2CH_2-O)_l-(\underset{\diagdown\,O\,\diagup}{CH-CH})_m-(CH_2-\underset{CN}{\underset{|}{CH}})_n$$

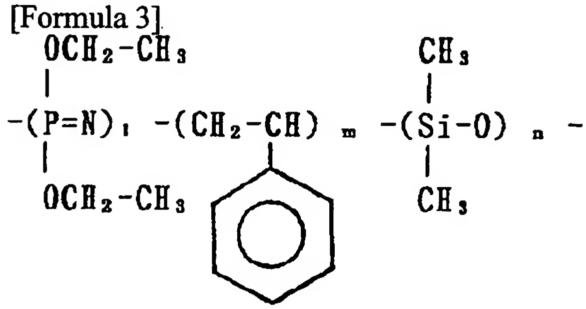
[0020]

[Formula 2]

$$-(CH_2CH_2-O)_n-(CH_2-CF_2)_m-(CH_2-CH_2)_l-$$

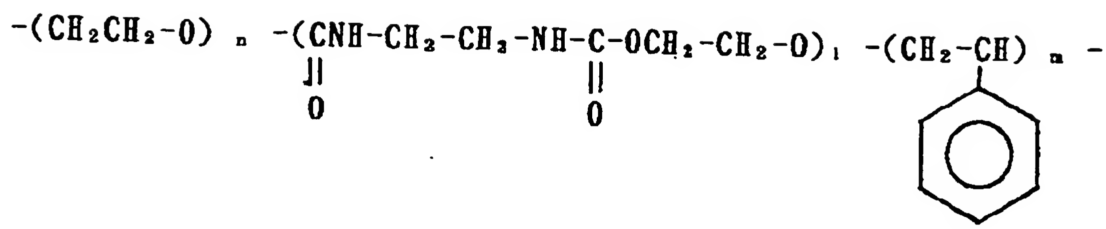
[0021]

[Formula 3]

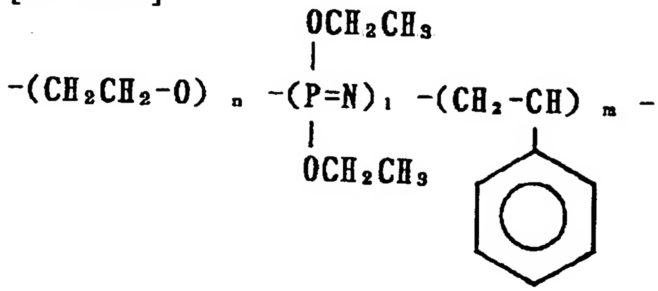


[0022]

[Formula 4]



[0023]
[Formula 5]



[0024]
[Formula 6]

$$-(CH_2CH_2-O)_n-(\underset{\displaystyle OCH_2CH_3}{\overset{\displaystyle OCH_2CH_3}{P}}=N)_l-(CH_2-CH_2-SO_2)_m-$$

[0025] [Solid electrolyte cell] The flat type solid electrolyte cells A1-A6 (1st cell; geometric capacity : 30 mAh/g-cell weight; cell size : 1.6mm in the diameter of 20mm, thickness) were assembled in order using a positive electrode, an above-mentioned negative electrode, and each above-mentioned solid polymer electrolyte.
[0026] (An example 7 - 12 : the 2nd cell) They are various kinds of 3 yuan copolymer films shown in Table 2 to propylene carbonate LiClO4 Flood with the solution (electrolytic solution) melted 1. one mol /, it was made to swell, and the macromolecule gel electrolyte was produced. In addition, all the weight ratios of the sinking-in **** electrolytic solution and each film were set to 4:1. Subsequently, solid electrolyte cells A7-A12 (the 2nd cell) were assembled like examples 1-6 except having used these macromolecule gel electrolytes.
[0027] (Example 1 of comparison) After melted the polyethylene-oxide [-(CH2-CH2-O) n-] 93 weight section of average molecular weight 60,000 [about] to the acetonitrile, prepared the solution, having added the LiClO4 7 weight section to this solution, having carried out the cast of this, having carried out reduced pressure drying on the petri dish made from stainless steel and removing an acetonitrile, stoving was carried out by 100 degreeC and the solid polymer electrolyte was produced. The solid electrolyte cell B1 was assembled like examples 1-6 except having used this solid polymer electrolyte.
[0028] (Examples 2-4 of comparison) LiClO4 Mixed solvent of the volume ratio 3:2 of ethylene carbonate and 1 and 2-dimethoxyethane (example 2 of comparison), Liquid electrolyte cell B-2-B4 were assembled in order to the mixed solvent (example 4 of comparison) of the volume ratio 3:1:1 of the mixed solvent (example 3 of comparison) of the volume ratio 3:2 of ethylene carbonate and a tetrahydrofuran or ethylene carbonate, 1 and 2-dimethoxyethane, and a tetrahydrofuran, using the solution melted 1. one mol /as the electrolytic solution. The nonwoven fabric made from polypropylene was used as separator.
[0029] (Example 5 of comparison) It is a polyethylene-oxide film to propylene carbonate LiClO4 Flood with the solution (electrolytic solution) melted 1. one mol /, it was made to swell, and the macromolecule gel electrolyte was produced. In addition, all the weight ratios of the sinking-in **** electrolytic solution and a polyethylene-oxide film were set to 4:1. Subsequently, solid-electrolyte-

cell B5 was assembled like examples 1-6 except having used this macromolecule gel electrolyte.

[0030] <Decomposition current> Using each electrolyte, the platinum electrode as an operation pole, and the lithium electrode as a counter electrode and a reference pole, the examination cell was assembled, the reduction current (decomposition current muA/cm2) when subsequently to 0 V pair reference pole (Li/Li+) setting up the potential of a platinum electrode was measured, and the difficulty of the resolvability of each electrolyte was investigated. It means that it is easy to disassemble an electrolyte, so that decomposition current is large. A result is shown in Table 1 and 2.

[0031]

[Table 1]

電池	高分子　又は溶媒	分解電流 ($\mu A/cm^2$)	50ｻｲｸﾙ目の放電容量 (mAh／g)
A1	ｴﾁﾚﾝｵｷｼﾄﾞ-ｱｸﾘﾛﾆﾄﾘﾙ-ｴﾎﾟｷｼ	5.3	22
A2	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｯ 化ﾋﾞﾆﾘﾃﾞﾝ-ｴﾁﾚﾝ	5.2	21
A3	ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ-ｼﾛｷｻﾝ	5.0	25
A4	ｳﾚﾀﾝ-ｴﾁﾚﾝｵｷｼﾄﾞ-ｽﾁﾚﾝ	4.9	20
A5	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ	5.0	24
A6	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾙﾎﾝ	4.5	19
B1	ﾎﾟﾘｴﾁﾚﾝｵｷｼﾄﾞ	15.2	10
B2	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+1,2-ｼﾞﾒﾄｷｼｴﾀﾝ	20.4	10
B3	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+ﾃﾄﾗﾋﾄﾞﾛﾌﾗﾝ	21.4	8
B4	ｴﾁﾚﾝｶｰﾎﾞﾈｰﾄ+1,2-ｼﾞﾒﾄｷｼｴﾀﾝ+ﾃﾄﾗﾋﾄﾞﾛﾌﾗﾝ	23.2	7

[0032]

[Table 2]

電池	高分子	電解液	分解電流 ($\mu A/cm^2$)	50ｻｲｸﾙ目の放電容量 (mAh／g)
A7	ｴﾁﾚﾝｵｷｼﾄﾞ-ｱｸﾘﾛﾆﾄﾘﾙ-ｴﾎﾟｷｼ	$LiClO_4$+PC	5.8	25
A8	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｯ 化ﾋﾞﾆﾘﾃﾞﾝ-ｴﾁﾚﾝ	$LiClO_4$+PC	5.8	26
A9	ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ-ｼﾛｷｻﾝ	$LiClO_4$+PC	5.5	25
A10	ｳﾚﾀﾝ-ｴﾁﾚﾝｵｷｼﾄﾞ-ｽﾁﾚﾝ	$LiClO_4$+PC	5.4	27
A11	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾁﾚﾝ	$LiClO_4$+PC	5.3	28
A12	ｴﾁﾚﾝｵｷｼﾄﾞ-ﾌｫｽﾌｧｾﾞﾝ-ｽﾙﾎﾝ	$LiClO_4$+PC	5.0	27
B5	ﾎﾟﾘｴﾁﾚﾝｵｷｼﾄﾞ	$LiClO_4$+PC	18.2	11

[0033] Table 1 shows that it is hard to decompose from decomposition current being small as compared with the conventional solid polymer electrolyte which produced the liquid electrolyte which produced the solid polymer electrolyte produced in the examples 1-6 in the examples 2-4 of comparison in the example 1 of comparison from the first. Moreover, Table 2 shows that it is hard to decompose from decomposition current being small as compared with the conventional macromolecule gel electrolyte which produced the macromolecule gel electrolyte produced in the examples 7-12 in the example 5 of comparison.

[0034] <50 Service capacity of a cycle eye> It is 0.5 mA/cm2 under a room temperature (25degreeC) about each cell. 0.5 mA/cm2 after charging to 3.20V The charge-and-discharge cycle examination which makes 1 cycle the process which discharges to 2.00V was performed, and the service capacity of 50 cycle eye was calculated. A result is shown in previous Table 1 and 2.

[0035] Decomposition current compares the solid electrolyte cells A1-A12 (this invention cell) using

the solid polymer electrolyte with decomposition current smaller than Table 1 and 2, or the macromolecule gel electrolyte with the cell B1 using the large solid polymer electrolyte, the liquid electrolyte, or the macromolecule gel electrolyte -: B5 (comparison cell), the service capacity of 50 cycle eye is large, and it turns out that it excels in the charge-and-discharge cycle property.

[Translation done.]